

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
16 August 2001 (16.08.2001)

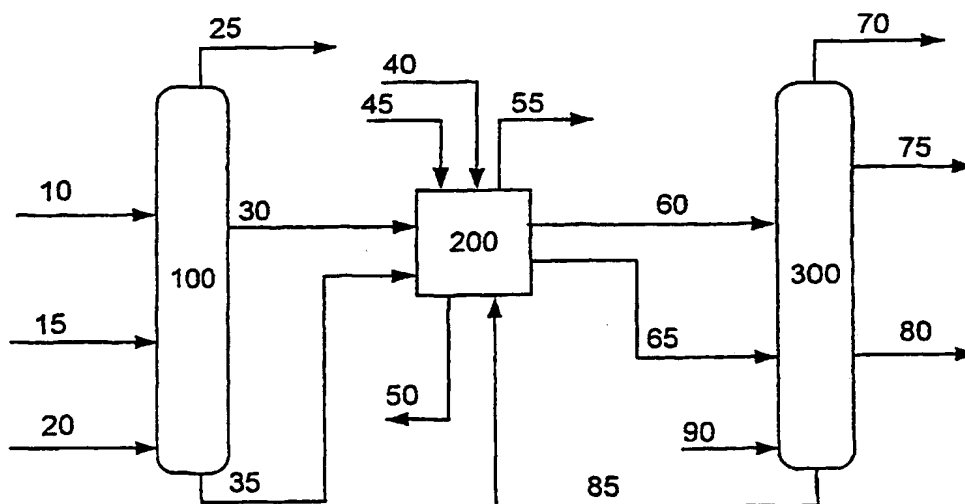
PCT

(10) International Publication Number
WO 01/59034 A2

- (51) International Patent Classification⁷: **C10L**
- (21) International Application Number: **PCT/US01/03845**
- (22) International Filing Date: **7 February 2001 (07.02.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
09/499,690 8 February 2000 (08.02.2000) **US**
- (63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:
US 09/466,690 (CON)
Filed on 8 February 2000 (08.02.2000)
- (71) Applicant (for all designated States except US): **SYN-TROLEUM CORPORATION [US/US];** Syntroleum Plaza, 1350 South Boulder, Suite 1100, Tulsa, OK 74119-3295 (US).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **TOMLINSON, Harvard, L., Jr. [US/US];** 21 East 26th Street, Tulsa, OK 74114 (US). **BRANCH, J., Russell [US/US];** 9801 Knoxville Avenue, Tulsa, OK 74137 (US).
- (74) Agents: **BELSER, Townsend, M., Jr. et al.;** Suite 800, 1990 M Street, N.W., Washington, DC 20036-3425 (US).
- (81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.**
- (84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**

[Continued on next page]

(54) Title: **MULTIPURPOSE FUEL/ADDITIVE**



(57) Abstract: A fuel or fuel additive composed predominantly, on a weight basis, of hydrocarbons in the C₉-C₂₂ range, and including material boiling above and below 700 degrees F. At least about 50 % by weight of the material boiling above 700 degrees F. has been subjected to treatment with hydrogen to saturate at least a portion of any aromatics and/or other unsaturates. The fuel or fuel additive comprises at least about 99, at least about 99.3 or at least about 99.5 % by weight of normal- and/or iso-paraffins based on the total weight of hydrocarbons; has less than about 500, or less than about 200, or less than about 100, or less than about 50, or substantially zero ppm of unsaturates, based on the total weight of fuel or fuel additive; has a cetane number of at least about 70, at least about 74 or at least about 75; and contains less than about 1 ppm, less than about 750 ppb, less than about 500 ppb or less than about 300 ppb each of S and N, based on the total weight of fuel or fuel additive.

WO 01/59034 A2



Published:

— *without international search report and to be republished
upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

MULTIPURPOSE FUEL/ADDITIVE

TECHNICAL FIELD

This invention relates to versatile hydrocarbon liquid materials. In certain embodiments, it relates to fuels and/or to blending agents for fuels. In preferred embodiments the fuels/blending agents are suitable for a variety of fuel applications, such as diesel fuel, fuel cell fuel, jet fuel, turbine fuel, boiler or furnace fuel, and they may be used in any other application in which they are useful. In a particularly preferred embodiment, the fuel/blending agent is predominantly composed of C₉-C₂₂ hydrocarbons synthesized in Fischer-Tropsch processing.

BACKGROUND OF THE INVENTION

Many small refineries, which cannot be upgraded due to unavailability or high cost of capital, are unable to economically and sufficiently reduce the sulphur content of moderately priced crudes when converting the latter to fuels. Operators of these plants are thus confronted with operating with costly sweet crude at marginal profit levels or operating with lower priced crudes of higher sulphur content and mixing the resultant products with blending agents of low or negligible sulphur content to produce environmentally acceptable fuels.

Contemporaneously, environmental standards for diesel fuels, particularly with respect to sulphur and other fuel components believed responsible for particulate emissions, are

progressively tightening. This has led to proposals for diesel fuels based on hydrocarbons produced through Fischer-Tropsch synthesis, which is capable of generating fuel liquids having very low sulphur contents.

5 As these events have unfolded, decades of research on fuel cells has progressed to the extent that city transit buses, powered by fuel cells, have now operated on a test basis. A variety of automakers are investing in research on application of fuel cells to automobiles and on fuels and fuel processors
10 for fuel cells.

 Burgeoning technical and environmental requirements applicable to fuels, and also to blending agents for producing such fuels, have led to the manufacture and availability of a wide variety of hydrocarbon fuels and to a number of different
15 forms of blending agents for use in them. Requirements for maintaining separate production procedures, production facilities, storage facilities and transportation and distribution facilities for many of these fuels increases the costs of the individual fuels. Thus, it has been suggested, and
20 research has been conducted, on production of multipurpose fuels. However, it is believed that the need for improved fuels and/or for multi-purpose fuels and fuel additives has outstripped available technology and that a need for such still exists. The purpose of the present invention is to fulfill
25 this need.

SUMMARY OF THE INVENTION

The invention provides a fuel or fuel additive, comprising hydrocarbons. These are composed predominantly, on a weight basis, of material in the C₉-C₂₂ range, and include material boiling above and below 700 degrees F. At least about 50% by weight of the material boiling above 700 degrees F. has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion of any aromatics and/or other unsaturates that may have been present therein. Moreover, the fuel or fuel additive comprises at least about 99, at least about 99.3 or at least about 99.5% by weight of normal- and/or iso- paraffins based on the total weight of hydrocarbons, and has less than about 500, or less than about 200, or less than about 100, or less than about 50, or substantially zero ppm of unsaturates, based on the total weight of said fuel or fuel additive. The latter also has a cetane number of at least about 70, at least about 74 or, at least about 75, and contains less than about 1 ppm, less than about 750 ppb, less than about 500 ppb or less than about 300 ppb each of S and N, based on the total weight of said fuel or fuel additive.

According to a preferred embodiment, the fuel or fuel additive hydrocarbon content is composed predominantly, or substantially, or entirely of material prepared by Fischer-Tropsch synthesis.

In yet another embodiment, the hydrocarbon content of the fuel or fuel additive has an iso- to normal- paraffin weight ratio in the range about 0.02:1 to about 20:1, or in the range

of about 0.1:1 to about 15:1, or in the range of about 0.5:1 to about 12:1.

In other embodiments, (a) at least about 50% by weight of the material boiling below 700 degrees F., or (b) substantially all of the material boiling above 700 degrees F., or (c) substantially all of the material boiling below 700 degrees F., or any combination thereof, has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion, a substantial portion, or substantially all, of any aromatics and/or other unsaturates that may have been present therein.

In still another embodiment, the fuel or fuel additive is composed predominantly, or substantially, or entirely of material prepared by Fischer-Tropsch synthesis, and substantially all of the material prepared by Fischer-Tropsch synthesis has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion, a substantial portion, or substantially all, of any unsaturates and/or alcohols that may have been present therein.

In particularly preferred embodiments, the fuel or fuel additive contains less than about 200, less than about 100, less than about 50 or substantially zero ppm of C₁₂-C₂₄ primary alcohol oxygenate, as oxygen, on a water free basis, based on the total weight of said fuel or fuel additive.

Embodiments are contemplated in which the fuel or fuel additive contains up to about 0.01%, or up to about 0.1%, or up to about 1% by weight of a lubricity improver, based on the total weight of said fuel or fuel additive.

There are also embodiments of the invention in which the fuel or fuel additive has a flash point, as measured by ASTM D-93 of at least about 80 degrees F., or at least about 100 degrees F., or at least about 120 degrees F, or at least about 150 degrees F.

In other embodiments, the fuel or fuel additive has a flash point, as measured by ASTM D-93, in the range of about 80 to about 150 degrees F., or in the range of about 90 to about 130 degrees F.

Among the important products of the invention are fuel cell fuel, diesel fuel, jet fuel, turbine fuel and furnace or boiler fuel according to the invention as broadly stated above, or in accord with any of the above-identified embodiments. Other important products include fuel cell fuel, diesel fuel, jet fuel, turbine fuel and furnace or boiler fuel comprising a fuel additive according to the invention as broadly stated above, or in accord with any of the above-identified embodiments.

Another particularly important embodiment is a multi-purpose fuel useful as fuel cell fuel and as diesel engine fuel and conforming to the invention as broadly stated above, or to any of the above-identified embodiments.

Yet another important embodiment is a fuel additive useable as a blending agent to be mixed with other fuel components to prepare multi-purpose fuel useful as fuel cell fuel and as diesel engine fuel.

Also contemplated are embodiments constituting multi-purpose fuel useful as fuel cell fuel, and as diesel engine

fuel, and as jet engine fuel, and as turbine fuel and as furnace or boiler fuel.

Also contemplated is a fuel additive useable as a blending agent to be mixed with other fuel components to prepare multi-purpose fuel useful as fuel cell fuel, and as diesel engine fuel, and as jet engine fuel, and as turbine fuel and as furnace or boiler fuel.

ADVANTAGES

All embodiments of the invention will not necessarily possess all of the same advantages. However, preferred embodiments of the invention will exhibit at least one or a combination of the following advantages.

Particularly preferred embodiments of the invention will be multipurpose fuels, useful in a variety of applications. For example, the invention includes embodiments that are useful as both diesel and fuel cell fuels.

Certain embodiments of the invention, characterized by very high cetane numbers, provide extremely smooth operation of diesel engines. Such engines, when operated respectively on conventional fuel and fuel according to the invention, can differ markedly in the sound levels they generate. The preferred high cetane fuel embodiments, with their shorter burning time, generate power more smoothly and quietly in diesel engines.

In certain of its embodiments, the invention provides multipurpose fuels of high hydrogen content characterized by containing at least about 99% by weight of paraffins, very

small quantities of unsaturates and very low levels of sulphur and nitrogen. Production of the fuels by hydrotreating of Fischer-Tropsch products provides a dependable and economical route for these fuel products.

5 These products, which may be derived from partially or fully hydrotreated hydrocarbon stocks, may in certain preferred embodiments be produced with substantially no amounts, or restricted amounts, of alcohols or primary alcohols. For example, in one embodiment, the products are free of C₁₂-C₂₄
10 primary oxygenates and, where appropriate, may be blended with any suitable lubricity improvers.

Both industry and government have focused on conventional gasoline and diesel as fuel cell fuels because they can be delivered using the present fuel distribution system and they
15 have relatively high hydrogen carrying capacity. EPA #2 diesel sold in the U.S. contains sulfur commonly in excess of 300 ppm and should be passed through a heated absorbent bed to remove sulfur compounds prior to being fed into a fuel cell fuel processor. No such absorbent bed is necessary when processing
20 multipurpose synthetic fuel. The elimination of this step will lower manufacturing and operating costs of fuel cell fuel processors. This multipurpose fuel will also be able to use the existing distribution infrastructure, affording it easier market access than other fuels under consideration for fuel
25 cells, such as methanol and compressed natural gas (CNG).

Typical EPA #2 diesel fuel typically contains greater than 30% aromatics and greater than 10% olefins, which are hydrogen-poor, and can reduce processor conversion efficiency.

Substantially eliminating aromatics decreases the propensity of carbon formation and potentially increases the efficiency of the reformer as well as the lifetime of the catalyst.

5 Still other advantages of the invention will become apparent to persons skilled in the art from use of the products of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

10 The single drawing is a schematic diagram of a manufacturing method for converting starting material to fuel or fuel additive in accord with the invention.

VARIOUS AND PREFERRED EMBODIMENTS

15 In general, all possible novel and non-obvious combinations of individual features of this disclosure represent embodiments of the present invention, whether originally claimed or not. Moreover, the invention includes other embodiments, combinations not disclosed herein, which fall within the scope of the patent claims or represent equivalents under the doctrine of equivalents. Thus, the embodiments disclosed below are merely illustrative.

20 The starting material used in production of the fuel and fuel additive herein may be any suitable stock of natural or synthetic origin. Preferably, the starting material is of Fischer-Tropsch origin, as will be more fully discussed below.

25 These stocks will be essentially hydrocarbon in content. Aromatics and other unsaturates, as well as sulphur and nitrogen, may be present. However, the preferred starting

materials are substantially unsaturated, substantially paraffinic Fischer-Tropsch products which are usually characterized by low levels of sulphur and nitrogen.

5 In theory, there is no lower or upper limit on the number of carbon atoms which may be present in the molecules of the starting material. However, the goal of the invention is production of fuel or fuel additives, including hydrocarbon material which is either within, throughout, or substantially conforming to the range of about C₉ to C₂₂. Thus, materials
10 substantially lighter and heavier than those desired in the final product may be absent from the starting material or, if present, will be removed during conversion of the starting material to final product.

Starting material may be produced from petroleum
15 fractions, for example, by distillation and/or flashing and/or stripping and/or other usual processing steps that have been applied in processing of such fractions. When the starting material is produced via Fischer-Tropsch processing, natural gas, gasified coal and/or other gaseous raw materials are
20 converted to synthesis gas, a mixture composed substantially of carbon monoxide and molecular hydrogen. This may be done, for example, by steam reforming, partial oxidation or autothermal reforming. The resultant synthesis gas is then utilized as feed stock for a Fischer-Tropsch reaction to make the starting
25 material.

In the Fischer-Tropsch reaction, any suitable catalyst can be used to convert the synthesis gas to Fischer-Tropsch liquids, which tend to be primarily paraffinic. Suitable

catalysts include those based on cobalt or iron as the primary catalytic material. The preferred catalyst is cobalt on any suitable support which may, for example, be silica, alumina, silica-alumina or Group VIB metal oxides, such as titania.

5 Promoters may also be present with the primary catalytic material, e.g. ruthenium, rhenium, titanium, zirconium or hafnium.

The product recovered from the Fischer-Tropsch catalytic reactor may, for example, be separated into various fractions.

10 A heavy Fischer-Tropsch liquid may, for example, be recovered and may be used or stored with or without intermediate hydrocracking and stabilization. A light Fischer-Tropsch liquid product, for example about C₄ to about C₂₈, may also be sent to storage or used. At room temperature, the light
15 Fischer-Tropsch liquid is in a liquid state and the heavy Fischer-Tropsch liquid is in a solid state. Water and low molecular weight alcohols, such as methanol and ethanol, can and preferably are stripped from the light Fischer-Tropsch liquids.

20 In one embodiment, the light Fischer-Tropsch liquids may be fractionated to produce starting material corresponding to the desired carbon number range of the ultimate fuel or fuel additive product, for example, about C₉ to about C₂₂ or some portion of this range. In another embodiment, which is
25 preferred, both light and heavy Fischer-Tropsch liquids, in a liquid state, and with a C number range exceeding C₂₂, and possibly also including components of less than C₉, is hydro treated in such a way as to adjust, or partially adjust the C

number range of the starting material to the desired C number range of the product. Further adjustment can be accomplished with the aid of fractionation.

Referring to the Figure, a light Fischer-Tropsch liquid 10 is introduced into a feed fractionator 100 along with a heavy Fischer-Tropsch liquid 20. Exemplary representations of streams 10 and 15 are provided in Table 1, below.

Description	Units	Range
Gas to Oil Ratio	SCF/Bbl	1500 - 7000
Liquid Hourly Space Velocity (LHSV)	hour ⁻¹	0.5 - 6.0
Catalyst Average Temperature (CAT)	°F	400 - 800
Hydrogen Partial Pressure	psia	300 - 1800
Hydrogen Chemical Consumption	SCF/Bbl	100 - 1000

The light Fischer Tropsch liquid 10 may or may not be a stabilized product. Fractionator 100 provides the necessary separation to produce an unstabilized light synthetic paraffin stream 25 composed predominantly of C9 and lesser carbon numbers, a C9-C17 middle distillate product 30, and a C18+ stream 35. Superheated steam 20 is provided to promote effective separation.

Middle distillate C9-C17 fraction 30 is then boosted to the operating pressure of hydrocracking reactor 200, mixed with

circulating hydrogen, and heated before being introduced into an active catalyst zone in the reactor. Likewise, C18+ heavy paraffin bottoms are boosted to the operating pressure of reactor 200, mixed with circulating hydrogen, and heated before
5 being introduced into an active catalyst zone of the reactor. Fractions 30 and 35 may or may not be fed into the same catalyst zone or chamber of hydrocracker 200.

The conversion reactions employed in the hydrocracker are hydrocracking (HC), hydroisomerization (HI), and hydrogenation
10 (HY). The catalysts employed to promote HC and HI are usually characterized by Group VIII base and/or noble metal(s) on silica-alumina supports of varying acidity and structure. HY may be accomplished utilizing less expensive Group VIII metals on inactive supports. Illustrative operating conditions for the
15 hydrocracker are found in Table 2, below.

Description	Test/Units	Light Oil	Heavy Oil
Specific Gravity	ASTM D-1298	0.763	0.818
Composition			
Paraffins	GC; wt. %	60 - 80	80 - 90
Olefins	GC; wt. %	10 - 35	2 - 15
Alcohols	GC; wt. %	1 - 5	1 - 5
Distillation	ASTM D-2887		
wt. %			
IBP	°F	-48	231
5	°F	224	574
10	°F	268	628
30	°F	383	756
50	°F	464	855
70	°F	547	925
90	°F	652	1077
95	°F	712	1152
FBP	°F	816	1250

Make-up hydrogen 40 is provided to replace hydrogen losses which may be caused by chemical consumption, solubility in products, discharge with purge gas and off gas 55, and leaks.

Wash water 45 is introduced into the reactor loop to reduce the build-up of undesirable compounds in the circulating hydrogen. A light hydrocrackate 60 and heavy hydrocrackate 65 are the two liquid hydrocarbon products from hydrocracker 200. A process water stream 50 is also produced.

Product fractionator 300 receives products 60 and 65 and operates in such a manner as to produce a C5 minus offgas 70, a C5-C9 light synthetic paraffin 75, a C9-C22 multi-purpose fuel 80 and an unconverted waxy oil stream 85. Superheated steam 90 is used in fractionator 300 in a manner similar to that in which it is used in fractionator 100. Stream 85 is provided to allow for recycling to adjust the cut point on the multi-purpose fuel while minimizing C9 minus yields.

Light synthetic paraffin stream 75 may or may not be considered stabilized, depending on its intended application. Multi-purpose fuel 80 is a very highly saturated paraffin product with ultra-low sulfur and nitrogen compounds that has a very low volatility. Table 3, below, provides some typical characteristics of the multi-purpose fuel.

Description	Test/Units	Multi-Purpose Fuel
Specific Gravity	ASTM D-4052	0.770
Composition		
Paraffins	HPLC, wt. %	>99%
Bromine Index	ASTM D-2710, mgBR ₂ /100g	<100
Aromatics	HPLC, wt. %	0 wt. %
Pour point	ASTM D-97, °C	-60 - 0
Cloud Point	ASTM D-2500, °C	-40 - 5
Viscosity, 40°C	ASTM D-445, cSt	1.8 - 2.5
Flash Point	ASTM D-93, °F	80 - 150
Cetane Number	ASTM D-613	>70
Distillation	ASTM D-86	
wt. %		
IBP	°F	320
5	°F	379
10	°F	390
30	°F	445
50	°F	490
70	°F	540
90	°F	600
95	°F	628
FBP	°F	643

Example 1

Preparing Multi-purpose Fuel

An F-T wax and the co-produced F-T oil were obtained and charged separately to a HC/HI reactor. For the F-T wax the conditions were as shown in column I of Table 4, below.

Description	Units	Column 1	Column 2
Gas to Oil Ratio	SCF/Bbl	2500	2500
LHSV (Total Feed)	hour ⁻¹	1.0	1.0
CAT	°F	700-740	695 - 710
Hydrogen Partial Pressure	psia	~1000	~1000
Hydrogen Chemical Consumption	SCF/Bbl	200 - 400	100 - 200
Mode		Recycle to Extinction	Once-through

Column 2 of Table 4 presents the F-T light oil reactor conditions. The products from the F-T wax and light oil were

fractionated and combined in the ratios that they were produced such that the final blend represented a contiguous run of both feed stocks. Product properties are shown in Table 5, below.

Description	Test/Units	Multi-Purpose Fuel
Specific Gravity	ASTM D-4052	0.7716
Composition		
Paraffins	HPLC, wt. %	>99%
Bromine Index	ASTM D-2710, mgBR ₂ /100g	220
Aromatics	HPLC, wt. %	0 wt. %
Pour point	ASTM D-97, °C	-36°C
Cloud Point	ASTM D-2500, °C	-23°C
Viscosity, 40°C	ASTM D-445, cSt	2.12 cSt
Flash Point	ASTM D-93, °F	149
Cetane Number	ASTM D-613	73.6
Distillation	ASTM D-86	
wt. %	°F	
IBP	°F	318
5	°F	384
10	°F	390
30	°F	442
50	°F	491
70	°F	541
90	°F	600
95	°F	627
FBP	°F	633

It should be noted that no HY catalyst was employed in the production of this example as witnessed by the Bromine Index. HY is a very fast reaction at even mild conditions. HY catalyst can be employed where desired to obtain still further reductions in unsaturates content.

Example 2

Demonstrating Multi-purpose Fuel in Fuel Cell Fuel Processor

The synthetic multi-purpose fuel described herein may be applied, as appropriate, as a direct fuel (introduced directly into a fuel cell) or as a feed stream for a fuel processor. The present example illustrates use of the fuel of the present invention as a feed stream for a proprietary fuel processor made by Northwest Power Systems (Bend, Oregon).

The determined hydrogen yield of this multi-purpose fuel is at least equal to that of conventional diesel fuel. During short-term tests, conventional petroleum-derived diesel fuel yielded sufficient hydrogen to produce 8.67 kilowatt hours of electric flow (kWh) from one gallon of fuel and the multi-purpose fuel according to the invention yielded sufficient hydrogen to produce 9.05 kWh from one gallon of fuel.

Example 3

Testing Multi-Purpose Fuel in Diesel Engine

The multipurpose fuel of the present invention was compared against EPA #2 diesel in emission tests using an unmodified heavy duty 5.9L Cummins engine on a test stand

(Table 6) and an unmodified heavy-light duty diesel vehicle with the same engine on a chassis dynamometer (Table 7).

Table 6:

5 Summary of regulated emissions from a 5.9 L Cummins B Engine on a test stand

	Test (g/bhp-hr)	HC	CO	NOx	Particu- lates
	EPA #2, average	0.10	1.30	4.00	0.10
10	multipurpose fuel, average	0.10	0.80	3.20	0.06
	% reduction	0	38	20	40

Table 7:

15 Summary of US06 Emissions from a heavy light-duty truck (2000 Dodge RAM 2500 with a 5.9 L Cummins) on a chassis

	Dynamometer Test (g/bhp-hr)	HC	CO	NOx	Particu- lates
20	EPA #2, average	0.19	0.70	5.24	0.11
25	multipurpose fuel, average	0.16	0.50	4.50	0.06
30	% reduction	16	29	14	45

These tests show that preferred embodiments of the invention can provide major emission reduction benefits. The fuel of the invention significantly reduced emissions from the 5.9L Cummins in both tests. None of these tests included engine timing
5 modifications which could have taken advantage of the significantly higher cetane of the present fuel.

CLAIMS

What is claimed is:

1. A fuel or fuel additive, comprising:
hydrocarbons which are composed predominantly, on a weight basis, of material in the C9-C22 range,
said hydrocarbons including material boiling above and below 700 degrees F.,
at least about 50% by weight of the material boiling above 700 degrees F. having been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion of any aromatics and/or other unsaturates that may have been present therein,
said fuel or fuel additive
comprising at least about 99, at least about 99.3 or at least about 99.5% by weight of normal- and/or iso-paraffins based on the total weight of hydrocarbons, having less than about 500, less than about 200, less than about 100, less than about 50, or substantially zero ppm of unsaturates, based on the total weight of said fuel or fuel additive,
having a cetane number of at least about 70, at least about 74 or at least about 75,
and containing less than about 1 ppm, less than about 750 ppb, less than about 500 ppb or less than about 300 ppb each of S and N, based on the total weight of said fuel or fuel additive.
2. A fuel or fuel additive according to claim 1 in which the hydrocarbon content thereof is composed

3 predominantly, or substantially, or entirely of material
4 prepared by Fischer-Tropsch synthesis.

1 3. A fuel or fuel additive according to claim 1 in which the
2 hydrocarbon content thereof has an iso- to normal-
3 paraffin weight ratio in the range about 0.02:1 to about
4 20:1, or in the range of about 0.1:1 to about 15:1, or in
5 the range of about 0.5:1 to about 12:1.

1 4. A fuel or fuel additive according to claim 1 in which at
2 least about 50% by weight of the material boiling below
3 700 degrees F. has been subjected to treatment with
4 hydrogen under conditions sufficient to saturate at least
5 a portion, a substantial portion, or substantially all, of
6 any aromatics and/or other unsaturates that may have been
7 present therein.

1 5. A fuel or fuel additive according to claim 1 in which
2 substantially all of the material boiling above 700
3 degrees F. has been subjected to treatment with hydrogen
4 under conditions sufficient to saturate at least a
5 portion, a substantial portion or substantially all, of
6 any aromatics and/or other unsaturates that may have been
7 present therein.

1 6. A fuel or fuel additive according to claim 1 in which
2 substantially all of the material boiling below 700
3 degrees F. has been subjected to treatment with hydrogen
4 under conditions sufficient to saturate at least a
5 portion, a substantial portion, or substantially all, of

any aromatics and/or other unsaturates that may have been present therein.

7. A fuel or fuel additive according to claim 2 in which substantially all of the material prepared by Fischer-Tropsch synthesis has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion, a substantial portion, or substantially all, of any unsaturates and/or alcohols that may have been present therein.

8. A fuel or fuel additive according to claim 1 which contains less than about 200, less than about 100, less than about 50 or substantially zero ppm of C12-C24 primary alcohol oxygenate, as oxygen, on a water free basis, based on the total weight of said fuel or fuel additive.

9. A fuel or fuel additive according to claim 1 which contains up to about 0.01%, or up to about 0.1%, or up to about 1% by weight of a lubricity improver, based on the total weight of said fuel or fuel additive.

10. A fuel or fuel additive according to claim 1 having a flash point, as measured by ASTM D-93 of at least about 80 degrees F., or at least about 100 degrees F., or at least about 120 degrees F, or at least about 150 degrees F.

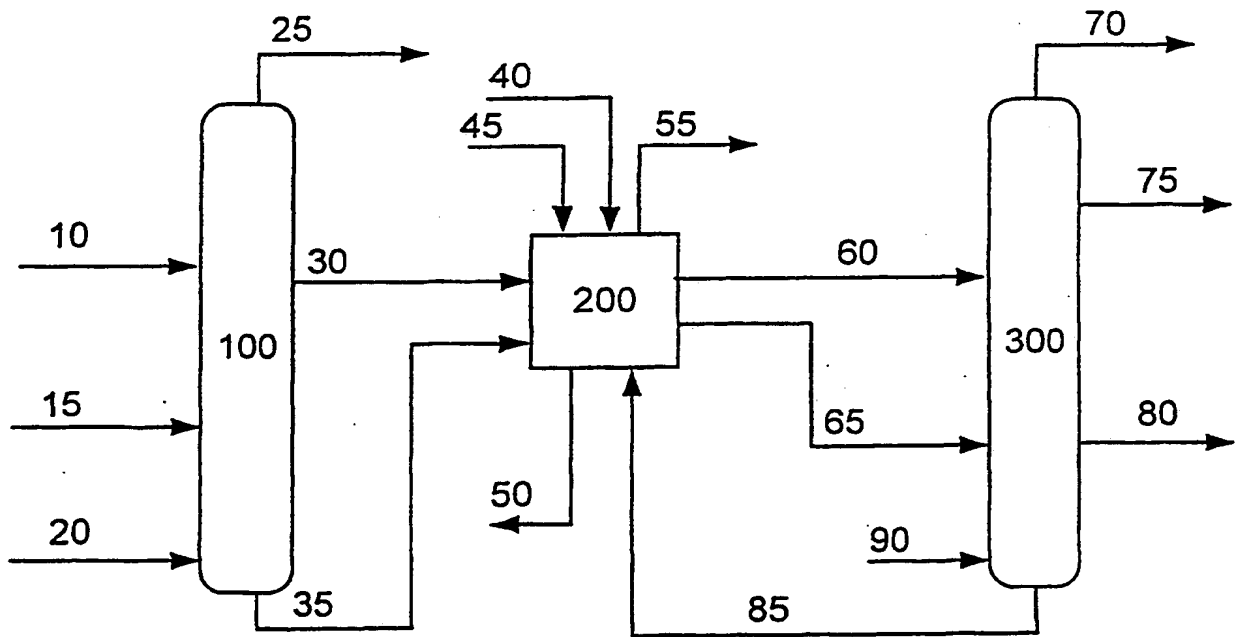
11. A fuel or fuel additive according to claim 1 having a flash point, as measured by ASTM D-93 in the range of about 80 to about 150 degrees F., or in the range of about 90 to about 130 degrees F.

- 1 12. A fuel cell fuel according to claim 1.
- 1 13. A fuel cell fuel comprising a fuel additive according to
2 claim 1.
- 1 14. A diesel fuel according to claim 1.
- 1 15. A diesel fuel comprising a fuel additive according to
2 claim 1.
- 1 16. A jet fuel according to claim 1.
- 1 17. A jet fuel comprising a fuel additive according to claim
2 1.
- 1 18. A turbine fuel according to claim 1.
- 1 19. A turbine fuel comprising a fuel additive according to
2 claim 1.
- 1 20. A furnace or boiler fuel according to claim 1.
- 1 21. A furnace or boiler fuel comprising a fuel additive
2 according to claim 1.
- 1 22. A fuel according to claim 1 constituting a multi-purpose
2 fuel useful as fuel cell fuel and as diesel engine fuel.
- 1 23. A fuel additive according to claim 1 useable as a blending
2 agent to be mixed with other fuel components to prepare

3 multi-purpose fuel useful as fuel cell fuel and as diesel
4 engine fuel.

1 24. A fuel according to claim 1 constituting a multi-purpose
2 fuel useful as fuel cell fuel, and as diesel engine fuel,
3 and as jet engine fuel, and as turbine fuel and as furnace
4 or boiler fuel.

1 25. A fuel additive according to claim 1 useable as a blending
2 agent to be mixed with other fuel components to prepare
3 multi-purpose fuel useful as fuel cell fuel, and as diesel
4 engine fuel, and as jet engine fuel, and as turbine fuel
5 and as furnace or boiler fuel.



THIS PAGE BLANK (USPTO)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
16 August 2001 (16.08.2001)

PCT

(10) International Publication Number
WO 01/59034 A3

(51) International Patent Classification⁷: C07C 5/10,
C10L 1/00, H01M 8/22

(21) International Application Number: PCT/US01/03845

(22) International Filing Date: 7 February 2001 (07.02.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/499,690 8 February 2000 (08.02.2000) US

(63) Related by continuation (CON) or continuation-in-part
(CIP) to earlier application:
US 09/466,690 (CON)
Filed on 8 February 2000 (08.02.2000)

(71) Applicant (for all designated States except US): SYN-
TROLEUM CORPORATION [US/US]; Syntroleum
Plaza, 1350 South Boulder, Suite 1100, Tulsa, OK
74119-3295 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): TOMLINSON,
Harvard, L., Jr. [US/US]; 21 East 26th Street, Tulsa,
OK 74114 (US). BRANCH, J., Russell [US/US]; 9801
Knoxville Avenue, Tulsa, OK 74137 (US).

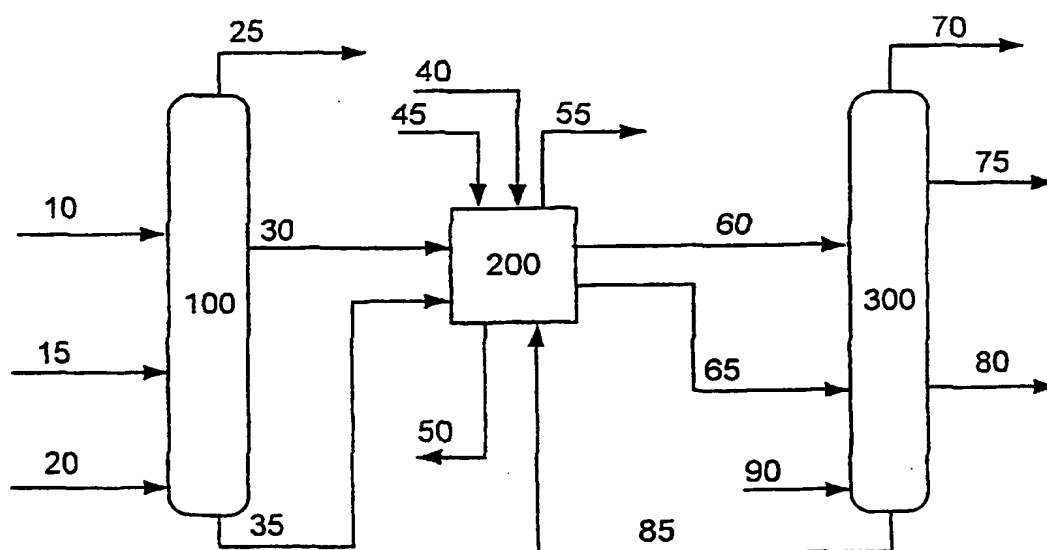
(74) Agent: PRIDDY, Robert, R.; Hall, Priddy, Myers &
Vande Sande, 10220 River Road, Suite 200, Potomac, MD
20854 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,

[Continued on next page]

(54) Title: MULTIPURPOSE FUEL/ADDITIVE



(57) Abstract: A fuel or fuel additive composed predominantly, on a weight basis, of hydrocarbons in the C9-C22 range, and including material boiling above and below 700 degrees F. At least about 50 % by weight of the material boiling above 700 degrees F. has been subjected to treatment with hydrogen to saturate at least a portion of any aromatics and/or other unsaturates. The fuel or fuel additive comprises at least about 99, at least about 99.3 or at least about 99.5 % by weight of normal- and/or iso-paraffins based on the total weight of hydrocarbons; has less than about 500, or less than about 200, or less than about 100, or less than about 50, or substantially zero ppm of unsaturates, based on the total weight of fuel or fuel additive; has a cetane number of at least about 70, at least about 74 or at least about 75; and contains less than about 1 ppm, less than about 750 ppb, less than about 500 ppb or less than about 300 ppb each of S and N, based on the total weight of fuel or fuel additive.



IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(88) Date of publication of the international search report:
7 February 2002

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/03845

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C07C 5/10; C10L 1/00; H01M 8/22

US CL : 208/950; 518/700, 715; 585/1; 429/12, 17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/950; 518/700, 715; 585/1; 429/12, 17

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST (CAS, USPAT, EPO, JPAT)

search terms: Fuels, multipurpose, Fischer Tropsch, hydrogenation, aromatics

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,689,031 A (BERLOWITZ et al) 18 November 1997, Fig. 1, col. 1, line 45 - col. 2, line 10; col. 2, line 35 - col. 3, line 55; col. 4, lines 10-20).	1-25
Y	US 5,686,196 A (SINGH et al) 11 November 1997, abstract, col. 1, lines 10-40.	12, 13, 16-25
Y, P	US H1,849 A (FOURIE et al) 02 May 2000, col. 1-2.	12, 13, 16-25
A	US 5,814,109 A (COOK et al) 29 September 1998.	1-25
A	US 5,733,941 A (WAYCUILIS) 31 March 1998.	1-25
A	US 5,807,413 A (WITTENBRINK et al) 15 September 1998.	1-25

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 AUGUST 2001

Date of mailing of the international search report

07 SEP 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

BEKIR L. YILDIRIM

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01703845

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,766,274 A (WITTENBRINK et al) 16 June 1998.	1-25
A	US 5,583,276 A (HELLRING et al) 10 December 1996.	1-25
A	US 4,973,453 A (AGEE) 27 November 1990.	1-25
A	US 4,605,680 A (BEUTHER et al) 12 August 1986.	1-25
Y	AHMED et al, "Gas-to-Liquids Synthetic Fuels for use in Fuel Cells: Reformability, Energy Density, and Infrastructure Compatibility", paper, Proceedings of the 3rd International Fuel Cell Conference, November 30 December 03, 1999, Nagoya, Japan, paper in its entirety.	12, 13, 16-25.
A	"Revolutionary Products from Shell MDS", Asian Oil & Gas Journal, March 1995. pp.16-20.	1-25

Form PCT/ISA/210 (continuation of second sheet) (July 1998)★